

# Studying variation of fundamental constants with molecules

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## I. INTRODUCTION

In this chapter we will discuss an application of precision molecular spectroscopy to the studies of the possible spatial and temporal variations of the fundamental constants. As we will see below, molecular spectra are mostly sensitive to two such dimensionless constants, namely the fine-structure constant  $\alpha = \frac{e^2}{\hbar c}$  and the electron-to-proton mass ratio  $\mu = m_e/m_p$  (note that some papers define  $\mu$  as an inverse value, i.e. proton-to-electron mass ratio). At present NIST gives following values of these constants [1]:  $\alpha^{-1} = 137.035999679(94)$  and  $\mu^{-1} = 1836.15267247(80)$ .

The fine-structure constant  $\alpha$  determines the strength of electromagnetic (and more generally electroweak) interactions. In principle, there is similar coupling constant  $\alpha_s$  for quantum chromodynamics (QCD). However, because of the highly nonlinear character of the strong interactions, this constant is not well defined. Therefore, the strength of the strong interactions is usually characterized by the parameter  $\Lambda_{\text{QCD}}$ , which has the dimension of mass and is defined as the position of the Landau pole in the logarithm for the running strong coupling constant,  $\alpha_s(r) = \text{const}/\ln(r\Lambda_{\text{QCD}}/\hbar c)$ , where  $r$  has dimension of length.

In the Standard Model (SM) there is another fundamental dimensional parameter — the Higgs vacuum expectation value (VEV), which determines electroweak unification scale. Electron mass  $m_e$  and quark masses  $m_q$  are proportional to the Higgs VEV. Consequently, the dimensionless parameters  $X_e = m_e/\Lambda_{\text{QCD}}$  and  $X_q = m_q/\Lambda_{\text{QCD}}$  link electroweak unification scale with strong scale. For the light quarks  $u$  and  $d$ ,  $X_q \ll 1$ . Because of that the proton mass  $m_p$  is proportional to  $\Lambda_{\text{QCD}}$  and  $X_e \propto \mu$ . Below we will use  $\mu$  instead of  $X_e$  because it is more directly linked to experimentally measured atomic and molecular observables.

Below we will show that huge enhancement of the relative variation happens in transitions between close atomic, molecular and nuclear energy levels. Recently several new cases were found, where the levels are very close and narrow. Large enhancement of the variation effects is also possible in cold collisions of atoms and molecules near Feshbach resonances.

We will start with general review of the present situation in the search of the variation of  $\alpha$  and  $\mu$ . After that we will discuss in more detail the results, which follow from the astrophysical observations of the opti-

cal and microwave spectra of molecules. Finally, we will describe possible laboratory experiments with molecules. This field is very new and there are no competitive laboratory results on time-variation with molecules yet (see, however, Sec. VII), but there are very promising proposals and several groups already started experiments.

The analysis of the data from Big Bang nucleosynthesis [2], quasar absorption spectra, and Oklo natural nuclear reactor give us the space-time variation of constants on the Universe lifetime scale, i.e. on times from few billion to more than ten billion years. Comparison of the frequencies of different atomic and molecular transitions in laboratory experiments gives us the present variation on the timescale from few months to few years. There is no model independent connection between variations on such different timescales. However, in order to compare the importance of different results, we will often assume linear time dependence of the constants. This way we can interpret all results in terms of time derivatives of the fundamental constants. Within this assumption, we can use quasar absorption spectra to obtain the best current limit on the variation of the mass ratio  $\mu$  and  $X_e$  [3]:

$$\dot{\mu}/\mu = \dot{X}_e/X_e = (1 \pm 3) \times 10^{-16} \text{ yr}^{-1}. \quad (1)$$

We can also combine this result with the atomic clock results [4] to get the best limit on variation of  $\alpha$  [5, 6, 7]:

$$\dot{\alpha}/\alpha = (-0.8 \pm 0.8) \times 10^{-16} \text{ yr}^{-1}. \quad (2)$$

Note that both limits (1) and (2) depend on the assumption of the linear time dependence of fundamental constants.

The Oklo natural reactor gives the best limit on the variation of  $X_s = m_s/\Lambda_{\text{QCD}}$  where  $m_s$  is the strange quark mass [8, 9, 10]:

$$|\dot{X}_s/X_s| < 10^{-18} \text{ yr}^{-1}. \quad (3)$$

Note that the Oklo data can not give us any limit on the variation of  $\alpha$  since the effect of  $\alpha$  there is much smaller than the effect of  $X_s$  and within the accuracy of the present theory should be neglected [10].

In addition to the time-variation, one can also consider spatial-variation of constants. Massive bodies (stars or galaxies) can also affect physical constants. In other words the fundamental constants may depend on the

gravitational potential, e.g.

$$\delta\alpha/\alpha = k_\alpha \delta(GM/rc^2), \quad (4)$$

where  $G$  is the gravitational constant and  $r$  is the distance from the mass  $M$ . The strongest limit on such variation:

$$k_\alpha + 0.17k_\mu = (-3.5 \pm 6) \times 10^{-7}, \quad (5)$$

is obtained in Ref. [6] from the measurements of the dependence of atomic frequencies on the distance from the Sun due to the ellipticity of the Earth's orbit [4, 11] (parameters  $k_\mu$  is defined by analogy with Eq. (4)). Below we will also discuss some other results, including those, which indicate nonzero variation of fundamental constants.

## II. THEORETICAL MOTIVATION

How changing physical constants and violation of local position invariance may occur? Light scalar fields very naturally appear in modern cosmological models, affecting parameters of SM including  $\alpha$  and  $\mu$  (for the whole list of SM parameters see [12]). Cosmological variations of these scalar fields should occur because of drastic changes of the composition of the Universe during its evolution.

Theories unifying gravity and other interactions suggest the possibility of spatial and temporal variation of physical “constants” in the Universe [13]. Moreover, there exists a mechanism for making all coupling constants and masses of elementary particles both space and time dependent, and influenced by local environment (see review [14]). Variation of coupling constants can be non-monotonic, such as damped oscillations, for instance.

These variations are usually associated with the effect of massless (or very light) scalar fields. One candidate is the dilaton: a scalar which appears in string theories together with graviton, in a massless multiplet of closed string excitations. Other scalars naturally appear in cosmological models, in which our Universe is a “brane” floating in a space of larger dimensions. The scalars are simply brane coordinates in extra dimensions. However, the only relevant scalar field recently discovered, the cosmological dark energy, so far does not show visible variations. Observational limits on the variations of physical constant given in Sec. I are quite stringent, allowing only scalar couplings, which are tiny in comparison with gravity.

A possible explanation was suggested by Damour *et al.* [15, 16] who pointed out that cosmological evolution of scalars naturally leads to their self-decoupling. Damour and Polyakov have further suggested that variations should happen when the scalars get excited by some physical change in the Universe, such as phase transitions, or other drastic changes in the equation of state of the Universe. They considered several of them, but since the time of their paper a new fascinating transition has been discovered: from matter dominated (decelerating)

era to dark-energy dominated (accelerating) era. It is a relatively recent event, corresponding to cosmological redshift  $z \approx 0.5$ , or the look-back time of approximately 5 billion years.

The time dependence of the perturbation related to this transition can be calculated, and it turned out [17, 18] that the self-decoupling process is effective enough to explain why after this transition the variation of constants is as small as observed in laboratory experiments at the present time, while being at the same time consistent with possible observations of the variations of the electromagnetic fine-structure constant at  $z \gtrsim 1$  [19, 20, 21].

## III. DEPENDENCE OF ATOMIC AND MOLECULAR SPECTRA ON $\alpha$ AND $\mu$

Atomic and molecular spectra are most naturally described in atomic units ( $\hbar = m_e = e = 1$ ), where energy is measured in Hartrees ( $1 \text{ Hartree} = \frac{e^4 m_e}{\hbar^2} = 2 \text{ Ry} = 219474.6313705(15) \text{ cm}^{-1}$ ). In these units nonrelativistic Schrödinger equation for an atom with infinitely heavy pointlike nucleus does not include any dimensional parameters. The dependence of the spectrum on  $\alpha$  appears only through relativistic corrections, which describe fine-structure, Lamb shift, etc. The dependence of atomic energies on  $\mu$  is known as isotope effect and is caused by finite nuclear mass and volume. There are even smaller corrections to atomic energies, which depend on both  $\alpha$  and  $\mu$  and are known as hyperfine structure.

One can argue that atomic energy unit itself depends on  $\alpha$  as it can be expressed as  $\alpha^2 m_e c^2$ , where  $m_e c^2$  is the rest energy of the free electron. However, experimental search for possible variation of fundamental constants consists in observing time-variations of the ratios of different transition frequencies to each other. In such ratios the dependence of the units on fundamental constants cancels out. Below we will use atomic units unless otherwise is explicitly stated.

Relativistic corrections to the binding energies of atomic valence electrons are of the order of  $\alpha^2 Z^2$ , where  $Z$  is atomic number and become quite large for heavy elements. For our purposes, it is convenient to present the dependence of atomic transition frequencies on  $\alpha^2$  in the form

$$\omega = \omega_0 + qx, \quad (6)$$

where  $x = (\frac{\alpha}{\alpha_0})^2 - 1 \approx \frac{2\delta\alpha}{\alpha}$  and  $\omega_0$  is a transition frequency for  $\alpha = \alpha_0$ . Rough estimates of  $q$ -factors can be obtained from simple one-particle models, but in order to obtain accurate values one has to account for electronic correlations and perform large-scale numerical calculations. Recently such calculations were made for many atoms and ions [22, 23, 24, 25, 26, 27, 28, 29].

Isotope effects in atoms are of the order of  $\mu \sim 10^{-3}$  and magnetic hyperfine structure roughly scales as

$\alpha^2 \mu Z g_{\text{nuc}} \sim 10^{-7} Z g_{\text{nuc}}$ , where  $g_{\text{nuc}}$  is nuclear  $g$ -factor. One has to keep in mind that  $g_{\text{nuc}}$  also depends on  $\mu$  and quark parameters  $X_q$ . This dependence has to be considered, when we compare, for example, the frequency of the hyperfine transition in  $^{133}\text{Cs}$  (Cs frequency standard) [5], or the hydrogen 21 cm hyperfine line [30, 31] to various optical transitions [5].

At present there are many very accurate experiments where different optical and microwave atomic clocks are compared to each other [4, 32, 33, 34, 35, 36, 37, 38, 39]. These experiments place strong limits on the time-variation of different combinations of  $\alpha$ ,  $\mu$ , and  $g_{\text{nuc}}$ . As we mentioned above, the limit on  $\alpha$ -variation (2) follows from the experiment [4] and the limit (1) in the assumption of linear time-dependence of all constants. A detailed discussion of atomic experiments can be found in recent reviews [40, 41].

On a cosmological timescale a comparison of the hyperfine transition in atomic hydrogen with optical transitions in ions, was done in Refs. [30, 31]. This method allows one to study time-variation of the parameter  $F = \alpha^2 g_p \mu$ , where  $g_p$  is proton  $g$ -factor. Analysis of the absorption spectra of nine quasars with redshifts  $0.23 \leq z \leq 2.35$  gave

$$\delta F/F = (6.3 \pm 9.9) \times 10^{-6}, \quad (7)$$

$$\dot{F}/F = (-6 \pm 12) \times 10^{-16} \text{ yr}^{-1}, \quad (8)$$

which is consistent with zero variation of  $\mu$  and  $\alpha$ .

Molecular spectroscopy opens additional possibilities to study variation of fundamental constants. It is known that  $\mu$  defines the scales of electronic, vibrational, and rotational intervals in molecular spectra,  $E_{\text{el}} : E_{\text{vib}} : E_{\text{rot}} \sim 1 : \mu^{1/2} : \mu$ . In addition to that, molecules also have fine and hyperfine structure,  $\Lambda$ -doubling, hindered rotations, etc. All these structures have different dependencies on fundamental constants. Obviously, comparison of these structures to each other allows the study of different combinations of fundamental constants.

The sensitivity to temporal variation of fundamental constants may be strongly enhanced in transitions between narrow close levels of different nature. Huge enhancement of the relative variation  $\delta\omega/\omega$  can be obtained in transition between almost degenerate levels in atoms [22, 24, 25, 42, 43], molecules [3, 44, 45, 46, 49], and nuclei [50, 51].

An interesting case of enhancement of the effect of variation of fundamental constants can be found in collisions of ultracold atoms and molecules near Feshbach resonances [52]. The scattering length  $A$  near the resonance is extremely sensitive to the  $\mu$ -variation:

$$\frac{\delta A}{A} = K \frac{\delta \mu}{\mu}, \quad (9)$$

where the enhancement factor  $K$  can be very large. For example, for Cs-Cs collisions  $K \sim 400$  [52]. Enhancement can be further increased by adjusting the position of the

resonance using external fields. Near a narrow magnetic or optical Feshbach resonance the enhancement factor  $K$  may be increased by many orders of magnitude.

Calculation of the factor  $K$  in Ref. [52] is based on the analytical formula for the scattering length derived in Ref. [53]. This formula is valid for an arbitrary interatomic potential with power long-range tail ( $1/r^6$  for neutral atoms), i.e. this result includes all unharmonic corrections.

To the best of our knowledge, it is the only suggested experiment on time-variation, where the observable is not frequency. Because of that, we have to find another parameter  $L$  of the dimension of length to compare  $A$  with. In Ref. [52] the scattering length was defined in atomic units ( $a_B$ ). It is important, however, that because of the large enhancement in Eq. (9), the possible dependence of  $L$  on  $\mu$  becomes irrelevant. For example, if we measure  $A$  in conventional units, meters, which are linked to Cs standard, then  $\delta L/L = -\delta\mu/\mu$ , and

$$\frac{\delta(A/L)}{(A/L)} = (K+1) \frac{\delta\mu}{\mu}. \quad (10)$$

As long as  $K \gg 1$  the dependence of the used units on fundamental constants can be neglected. Below we will discuss several other experiments with huge enhancement factors, where this argument can be also applied.

#### IV. ASTROPHYSICAL OBSERVATIONS OF THE SPECTRUM OF $\text{H}_2$

$\text{H}_2$  is the most common molecule in the Universe and its UV spectra have been used for the studies of the possible  $\mu$ -variation for a long time. For a given electronic transition, the frequency of each rovibrational line has different dependence on  $\mu$  [54, 55]. Therefore, comparison of rovibrational frequencies from astrophysics with laboratory observations can give information on  $\mu$ .

In the adiabatic approximation, the rovibrational levels of the electronic state  $\Lambda$  with vibrational and rotational quantum numbers  $v$  and  $J$  are given by the Dunham expression [56]:

$$E(v, J) = \sum_{k,l \geq 0} Y_{k,l} \left(v + \frac{1}{2}\right)^k [J(J+1) - \Lambda^2]^l, \quad (11)$$

where each term depends on  $\mu$  in a following way:

$$Y_{k,l} \propto \mu^{l+k/2}. \quad (12)$$

Because of the smallness of the parameter  $\mu$ , coefficients  $Y_{k,l}$  rapidly decrease with both  $k$  and  $l$ , and for small  $v$  and  $J$ , we have the usual vibrational ( $k=1$ ) and rotational ( $l=1$ ) terms. The zero term of this expansion ( $k=l=0$ ) corresponds to the electronic energy.

One can define the sensitivity coefficient  $K_i$  for each rovibrational transition  $i$  of a given electronic band  $e-g$

[55]:

$$K_i \equiv \left( \frac{d\nu_i}{\nu_i} \right) / \left( \frac{d\mu}{\mu} \right) = \frac{\mu}{E_e - E_g} \left( \frac{dE_e}{d\mu} - \frac{dE_g}{d\mu} \right), \quad (13)$$

where both energies are given by expansion (11). The sign of  $K_i$  depends on the rovibrational energies of the excited ( $e$ ) and ground ( $g$ ) states (in the absorption spectra of the quasars only transitions from the ground electronic state are seen). The electronic energy, presented by the term  $Y_{0,0}$ , dominates the expansion and the coefficients  $K_i$  are rather small. Typically they are on the order  $10^{-2}$ , but can reach 0.05 for large values of the quantum numbers  $v$  and  $J$ .

The coefficients of expansion (11) can be found by fitting experimental spectra. After that the sensitivity coefficients  $K_i$  are found from Eqs. (12) and (13). Some rovibrational levels of different electronic excited states appear to be very close. For such levels additional non-adiabatic corrections can be included within the two-level approximation [57].

If there is  $\mu$ -variation  $\Delta\mu$ , this would lead to a difference in observed redshifts  $z_i$  for different lines:

$$\zeta_i \equiv \frac{z_i - z_{q,abs}}{1 + z_{q,abs}} = -\frac{\Delta\mu}{\mu} K_i. \quad (14)$$

By plotting the reduced redshifts  $\zeta_i$  against the sensitivity coefficients  $K_i$ , one can estimate  $\Delta\mu/\mu$ . The most recent study [20] of the possible  $\mu$ -variation using astrophysical data on  $H_2$  was based on the observation of the two quasar absorption systems with redshifts  $z_{q,abs} = 3.02$  and  $2.59$ . An analysis of the data on 76 lines from two UV bands of  $H_2$  gave the following result:

$$\frac{\Delta\mu}{\mu} = (-20 \pm 6) \times 10^{-6}. \quad (15)$$

This result indicates, at a  $3.5\sigma$  confidence level, that  $\mu$  has increased during the past 12 billion years. Assuming linear time-dependence we can rewrite Eq. (15) as

$$\frac{\dot{\mu}}{\mu} = (17 \pm 5) \times 10^{-16} \text{ yr}^{-1}. \quad (16)$$

This has to be compared with the ammonia result (1), which corresponds to a timescale about 6.5 billion years and is discussed in more detail in Sec. VI.

## V. ASTROPHYSICAL OBSERVATIONS OF MICROWAVE MOLECULAR SPECTRA

In the previous section we discussed astrophysical observations of UV spectra of  $H_2$ . The corresponding absorption bands are very strong and can be observed even for objects with very high redshifts. On the other hand,

as we have seen, the sensitivity coefficients  $K_i$  in Eq. (13) are rather small. This is because of the relative smallness of rovibrational energy compared to the total transition energy. Thus, it may be useful to study microwave spectra of molecules, where the relative frequency variations due to varying constants are larger.

### A. Rotational spectra

In 1996 Varshalovich and Potekhin [58] compared redshifts for microwave rotational transitions ( $J = 3 \rightarrow J = 2$ ) and ( $J = 2 \rightarrow J = 1$ ) in the CO molecule with redshifts of optical lines of light atomic ions from the same astrophysical objects at redshifts  $z = 2.286$  and  $z = 1.944$ . As long as atomic frequencies are independent on  $\mu$  and rotational transition frequencies are proportional to  $\mu$ , this comparison allowed to set the following limits on variation of  $\mu$ :

$$\frac{\delta\mu}{\mu} = (-0.6 \pm 3.7) \times 10^{-4} \quad \text{at } z = 2.286, \quad (17a)$$

$$\frac{\delta\mu}{\mu} = (-0.7 \pm 1.0) \times 10^{-4} \quad \text{at } z = 1.944. \quad (17b)$$

In the same paper [58], the authors compared the ( $J = 0 \rightarrow J = 1$ ) CO absorption line with the 21 cm hydrogen line for an object with  $z = 0.2467$ . They did not find a significant difference in respective redshifts and interpreted this result as yet another limit on variation of  $\mu$ . However, as we mentioned above, the frequency of the hydrogen hyperfine line is proportional to  $\alpha^2 \mu g_p$ , and this result actually places limit on the variation of the parameter  $F = \alpha^2 g_p$  [59]. Recently a similar analysis was performed by Murphy *et al.* [60] using more accurate data for the same object at  $z = 0.247$  and for a more distant object at  $z = 0.6847$ , and the following limits were obtained:

$$\frac{\delta F}{F} = (-2.0 \pm 4.4) \times 10^{-6} \quad \text{at } z = 0.2467, \quad (18a)$$

$$\frac{\delta F}{F} = (-1.6 \pm 5.4) \times 10^{-6} \quad \text{at } z = 0.6847. \quad (18b)$$

The object at  $z = 0.6847$  is associated with the gravitational lens toward quasar B0218+357 and corresponds to the backward time  $\sim 6.5$  Gyr. This object was also used by other authors, as will be discussed in Sec. VB and Sec. VI.

### B. The 18 cm transitions in OH

Let us consider transitions between hyperfine substates of the  $^2\Pi_{3/2}$  ground-state  $\Lambda$ -doublet in the OH molecule [61, 62, 63]. The  $\Lambda$ -doubling for  $^2\Pi_{3/2}$  states appears in the third order in the Coriolis interaction and the corresponding energy interval is inversely proportional to the

spin-orbit splitting between the  $^2\Pi_{3/2}$  and  $^2\Pi_{1/2}$  states, i.e., it scales as  $\mu^3\alpha^{-2}$ , while the hyperfine structure intervals scale as  $\alpha^2\mu g_{\text{nuc}}$ . Therefore, the ratio of the hyperfine interval to the  $\Lambda$ -doubling interval depends on the combination  $\tilde{F} = \alpha^4\mu^{-2}g_{\text{nuc}}$ . Higher-order corrections modify this parameter to the form  $\tilde{F} = \alpha^{3.14}\mu^{-1.57}g_{\text{nuc}}$  [64].

The hyperfine-structure splitting for the OH molecule is approximately 50 MHz and is much smaller than  $\Lambda$ -doubling interval, which is about 1700 MHz. Because of that, it is actually easier to compare the  $\Lambda$ -doubling transitions in OH to the 21 cm hydrogen line, or to rotational lines of the HCO<sup>+</sup> molecule [61, 62, 63, 64].

The most stringent limit on the variation of  $\tilde{F}$  was obtained in Ref. [64] from observations of the  $z = 0.6847$  gravitational lens:

$$\Delta\tilde{F}/\tilde{F} = (0.44 \pm 0.36^{\text{stat}} \pm 1.0^{\text{syst}}) \times 10^{-6}, \quad (19)$$

where systematic error mostly accounts for the possible Doppler noise, i.e. for the possible difference in the velocity distributions of different molecules in a molecular cloud.

The laboratory frequencies of the OH  $\Lambda$ -doublet were recently remeasured with higher precision using cold molecules produced by a Stark decelerator [65]. That may become important for future astrophysical measurements with higher accuracy.

## VI. LIMIT ON TIME-VARIATION OF $\mu$ FROM INVERSION SPECTRUM OF AMMONIA

Several years ago, van Veldhoven *et al.* suggested to use decelerated molecular beam of ND<sub>3</sub> to search for the variation of  $\mu$  in laboratory experiments [46]. The ammonia molecule has a pyramidal shape and the inversion frequency depends on the exponentially small probability of tunneling of the three hydrogen (or deuterium) atoms through the potential barrier [66]. Because of that, it is very sensitive to any changes of the parameters of the system, particularly to the reduced mass for this vibrational mode. The authors of Ref. [46] found that for ND<sub>3</sub> molecule,  $\delta\omega/\omega = -5.6\delta\mu/\mu$ . Therefore, the inversion frequency of ND<sub>3</sub> is nearly an order of magnitude more sensitive to  $\mu$ -variation than typical molecular vibrational frequencies (note that Ref. [46] contains a misprint in the sign of the effect).

However, even such enhanced sensitivity is insufficient to make the laboratory experiment on the time-variation of  $\mu$  using conventional molecular beams competitive. Stark-deceleration was used in Ref. [46] to slow down the beam to 52 m/s. Still, a much slower beam, or a fountain is necessary to increase the sensitivity by several orders of magnitude before a competitive experiment can be performed. The work in this direction is in progress [67].

On the other hand, an only slightly smaller enhancement also exists for the inversion spectrum of NH<sub>3</sub>, which

is often seen in astrophysics, even for high  $z$  objects. This fact was used in [3] to place the limit (1), which we will now discuss in some detail. The inversion vibrational mode of ammonia is described by a double-well potential with the first two vibrational levels lying below the barrier. Because of the tunneling, these two levels are split in inversion doublets. The lower doublet corresponds to the wavelength  $\lambda \approx 1.25$  cm and is used in ammonia masers. Molecular rotation leads to the centrifugal distortion of the potential curve. Because of that, the inversion splitting depends on the rotational angular momentum  $J$  and its projection  $K$  on the molecular symmetry axis:

$$\omega_{\text{inv}}(J, K) = \omega_{\text{inv}}^0 - c_1 [J(J+1) - K^2] + c_2 K^2 + \dots, \quad (20)$$

where we omitted terms with higher powers of  $J$  and  $K$ . Numerically,  $\omega_{\text{inv}}^0 \approx 23.787$  GHz,  $c_1 \approx 151.3$  MHz, and  $c_2 \approx 59.7$  MHz.

In addition to the rotational structure (20) the inversion spectrum includes much smaller hyperfine structure. For the main nitrogen isotope  $^{14}\text{N}$ , the hyperfine structure is dominated by the electric quadrupole interaction ( $\sim 1$  MHz) [68]. Because of the dipole selection rule  $\Delta K = 0$  the levels with  $J = K$  are metastable and in laboratory beam experiments the width of the corresponding inversion lines is usually determined by collisional broadening. In astrophysics the lines with  $J = K$  are also narrower and stronger than others, but the hyperfine structure for spectra with high redshifts is still unresolved.

For our purposes it is important to know how the parameters in Eq. (20) depend on fundamental constants. The molecular electrostatic potential in atomic units does not depend on fundamental constants (here we neglect small relativistic corrections which give a weak  $\alpha$  dependence). Therefore, the inversion frequency  $\omega_{\text{inv}}^0$  and constants  $c_{1,2}$  are functions of  $\mu$  only. Note that the coefficients  $c_i$  depend on  $\mu$  through the reduced mass of the inversion mode and because they are inversely proportional to the molecular moments of inertia. This implies a different scaling of  $\omega_{\text{inv}}^0$  and  $c_i$  with  $\mu$ .

The inversion spectrum (20) can be approximately described by the following Hamiltonian:

$$H_{\text{inv}} = -\frac{1}{2M_1}\partial_x^2 + U(x) + \frac{1}{I_1(x)} [J(J+1) - K^2] + \frac{1}{I_2(x)} K^2, \quad (21)$$

where  $x$  is the distance from N to the H-plane,  $I_1$ ,  $I_2$  are moments of inertia perpendicular and parallel to the molecular axis, correspondingly, and  $M_1$  is the reduced mass for the inversion mode. If we assume that the length  $d$  of the N—H bond does not change during inversion, then  $M_1 = 2.54 m_p$  and

$$I_1(x) \approx \frac{3}{2} m_p d^2 [1 + 0.2(x/d)^2], \quad (22)$$

$$I_2(x) \approx 3 m_p d^2 [1 - (x/d)^2]. \quad (23)$$

The dependence of  $I_{1,2}$  on  $x$  generates correction to the potential energy of the form  $C(J, K)x^2\mu$ . This changes the vibrational frequency and the effective height of the potential barrier, therefore changing the inversion frequency  $\omega_{\text{inv}}$  given by Eq. (20).

Following Ref. [69] we can write the potential  $U(x)$  in Eq. (21) in the following form:

$$U(x) = \frac{1}{2}kx^2 + b\exp(-cx^2). \quad (24)$$

Fitting vibrational frequencies for  $\text{NH}_3$  and  $\text{ND}_3$  gives  $k \approx 0.7598$  a.u.,  $b \approx 0.05684$  a.u., and  $c \approx 1.3696$  a.u. Numerical integration of the Schrödinger equation with the potential (24) for different values of  $\mu$  gives the following result:

$$\frac{\delta\omega_{\text{inv}}^0}{\omega_{\text{inv}}^0} \approx 4.46 \frac{\delta\mu}{\mu}. \quad (25)$$

It is instructive to reproduce this result from an analytical calculation. In the WKB approximation the inversion frequency is estimated as [70]:

$$\begin{aligned} \omega_{\text{inv}}^0 &= \frac{\omega_{\text{vib}}}{\pi} \exp(-S) \\ &= \frac{\omega_{\text{vib}}}{\pi} \exp\left(-\frac{1}{\hbar} \int_{-a}^a \sqrt{2M_1(U(x) - E)} dx\right), \end{aligned} \quad (26a)$$

$$(26b)$$

where  $\omega_{\text{vib}}$  is the vibrational frequency of the inversion mode,  $S$  is the action in units of  $\hbar$ ,  $x = \pm a$  are classical turning points for the energy  $E$ . For the lowest vibrational state  $E = U_{\text{min}} + \frac{1}{2}\omega_{\text{vib}}$ . Using the experimental values  $\omega_{\text{vib}} = 950 \text{ cm}^{-1}$  and  $\omega_{\text{inv}} = 0.8 \text{ cm}^{-1}$ , we get  $S \approx 5.9$ .

Expression (26b) allows one to calculate the dependence of  $\omega_{\text{inv}}^0$  on the mass ratio  $\mu$ . Let us present  $S$  in the following form:  $S = A\mu^{-1/2} \int_{-a}^a \sqrt{U(x) - E} dx$ , where  $A$  is a numerical constant and the square root depends on  $\mu$  via  $E$ :

$$\frac{d\omega_{\text{inv}}^0}{d\mu} = \omega_{\text{inv}}^0 \left( \frac{1}{2\mu} - \frac{dS}{d\mu} \right) \quad (27a)$$

$$= \omega_{\text{inv}}^0 \left( \frac{1}{2\mu} - \frac{\partial S}{\partial \mu} - \frac{\partial S}{\partial E} \frac{\partial E}{\partial \mu} \right). \quad (27b)$$

It is easy to see that  $\partial S / \partial \mu = -S / 2\mu$ . The value of the third term in Eq. (27b) depends on the form of the potential barrier:

$$\frac{\partial S}{\partial E} = -\frac{q}{4} \frac{S}{U_{\text{max}} - E}, \quad (28)$$

where for a square barrier  $q = 1$ , and for a triangular barrier  $q = 3$ . For a more realistic barrier shape,  $q \approx 2$ . Using the parametrization (24) to determine  $U_{\text{max}}$  we

get:

$$\frac{\delta\omega_{\text{inv}}^0}{\omega_{\text{inv}}^0} \approx \frac{\delta\mu}{2\mu} \left( 1 + S + \frac{S}{2} \frac{\omega_{\text{vib}}}{U_{\text{max}} - E} \right) = 4.4 \frac{\delta\mu}{\mu}, \quad (29)$$

which is close to the numerical result (25).

We see that the inversion frequency of  $\text{NH}_3$  is an order of magnitude more sensitive to the change of  $\mu$  than typical vibrational frequencies. The reason for this is clear from Eq. (29): it is the large value of the action  $S$  for the tunneling process.

Using Eqs. (21) – (23) one can also find the dependence on  $\mu$  of the constants  $c_{1,2}$  in Eq. (20) [3]:

$$\frac{\delta c_{1,2}}{c_{1,2}} = 5.1 \frac{\delta\mu}{\mu}. \quad (30)$$

It is clear that the above consideration is directly applicable to  $\text{ND}_3$ , where the inversion frequency is 15 times smaller and Eq. (26b) gives  $S \approx 8.4$ . According to Eq. (29), this leads to a somewhat higher sensitivity of the inversion frequency to  $\mu$  in agreement with Ref. [46]:

$$\text{ND}_3 : \begin{cases} \frac{\delta\omega_{\text{inv}}}{\omega_{\text{inv}}} \approx 5.7 \frac{\delta\mu}{\mu}, \\ \frac{\delta c_2}{c_2} \approx 6.2 \frac{\delta\mu}{\mu}. \end{cases} \quad (31)$$

We see from Eqs. (25) and (30) that the inversion frequency  $\omega_{\text{inv}}^0$  and the rotational intervals  $\omega_{\text{inv}}(J_1, K_1) - \omega_{\text{inv}}(J_2, K_2)$  have different dependencies on  $\mu$ . In principle, this allows one to study time-variation of  $\mu$  by comparing different intervals in the inversion spectrum of ammonia. For example, if we compare the rotational interval to the inversion frequency, then Eqs. (25) and (30) give:

$$\frac{\delta\{\omega_{\text{inv}}(J_1, K_1) - \omega_{\text{inv}}(J_2, K_2)\} / \omega_{\text{inv}}^0}{\{\omega_{\text{inv}}(J_1, K_1) - \omega_{\text{inv}}(J_2, K_2)\} / \omega_{\text{inv}}^0} = 0.6 \frac{\delta\mu}{\mu}. \quad (32)$$

The relative effects are substantially larger if we compare the inversion transitions with the transitions between the quadrupole and magnetic hyperfine components. However, in practice, this method will not work because of the smallness of the hyperfine structure compared to typical linewidths in astrophysics.

Again, as in the case of  $\Lambda$ -doubling in OH molecule, it is more promising to compare the inversion spectrum of  $\text{NH}_3$  with rotational spectra of other molecules, where

$$\frac{\delta\omega_{\text{rot}}}{\omega_{\text{rot}}} = \frac{\delta\mu}{\mu}. \quad (33)$$

In astrophysics any frequency shift is related to a corresponding apparent redshift:

$$\frac{\delta\omega}{\omega} = -\frac{\delta z}{1+z}. \quad (34)$$

According to Eqs. (25) and (33), for a given astrophysical object with  $z = z_0$  variation of  $\mu$  leads to a change of the

apparent redshifts of all rotational lines  $\delta z_{\text{rot}} = -(1 + z_0) \delta\mu/\mu$  and the corresponding shifts of all inversion lines of ammonia are:  $\delta z_{\text{inv}} = -4.46(1 + z_0) \delta\mu/\mu$ . Therefore, comparing the apparent redshift  $z_{\text{inv}}$  for  $\text{NH}_3$  with the apparent redshifts  $z_{\text{rot}}$  for rotational lines we can find  $\delta\mu/\mu$ :

$$\frac{\delta\mu}{\mu} = 0.289 \frac{z_{\text{rot}} - z_{\text{inv}}}{1 + z_0}. \quad (35)$$

High-precision data on the redshifts of  $\text{NH}_3$  inversion lines exist for the already mentioned object B0218+357 at  $z \approx 0.6847$  [71]. Comparing them with the redshifts of rotational lines of  $\text{CO}$ ,  $\text{HCO}^+$ , and  $\text{HCN}$  molecules from Ref. [72] one can get the following conservative limit from Eq. (35):

$$\frac{\delta\mu}{\mu} = (-0.6 \pm 1.9) \times 10^{-6}. \quad (36)$$

Taking into account that the redshift  $z \approx 0.68$  for the object B0218+357 corresponds to the look-back time of about 6.5 Gyr, this limit translates into the most stringent present limit (1) for the variation rate  $\dot{\mu}/\mu$ .

## VII. EXPERIMENT WITH $\text{SF}_6$

Now we switch to laboratory molecular experiments on time-variation. We start with the recent experiment on two-photon vibrational transition ( $v = 0, J = 4$ )  $\rightarrow$  ( $v = 2, J = 3$ ) in  $\text{SF}_6$  [47]. This is a Ramsey-type experiment with a supersonic beam of  $\text{SF}_6$  molecules. The beam velocity  $u = 400$  m/s and the length of the interaction region  $D = 1$  m corresponds to the linewidth of  $u/2D = 200$  Hz.

A  $\text{CO}_2$  laser was used to drive the two-photon transition and its frequency was controlled by a Cs standard [48]. This means, that the vibrational frequency  $\omega_{\text{vib}}$  in  $\text{SF}_6$  was compared with the hyperfine transition frequency  $\omega_{\text{hfs}}$  in Cs. Therefore, the experiment was sensitive to the combination of fundamental constants  $F = g_{\text{nuc}}\mu^{-1/2}\alpha^{2.83}$ . Measurements continued for 18 months, and the following result was obtained:

$$\dot{F}/F = (1.4 \pm 3.2) \times 10^{-14} \text{ yr}^{-1}. \quad (37)$$

This limit is weaker, than the most stringent limits obtained with atomic clocks. On the other hand, it constrains a different combination of fundamental parameters. Most importantly, in atomic experiments the parameters  $g_n$  and  $\mu$  always go as a product  $g_n\mu$ , while here we have combination  $g_n\mu^{-1/2}$ . That allows to combine atomic results [4, 35, 37] with limit (37) to obtain the best laboratory limit on  $\mu$ -variation:

$$\dot{\mu}/\mu = (3.4 \pm 6.5) \times 10^{-14} \text{ yr}^{-1}. \quad (38)$$

This limit is significantly weaker than astrophysical limit

(1), but there are good chances that it will be soon significantly improved.

## VIII. CLOSE NARROW LEVELS IN DIATOMIC MOLECULES

In this section we focus on very close narrow levels of different nature in diatomic molecules. Such levels may occur due to cancelation between either hyperfine and rotational structures [45], or between the fine and vibrational structures of the electronic ground state [49]. The intervals between the levels correspond to microwave frequency range convenient for experiments and the level widths are very small, typically  $\sim 10^{-2}$  Hz. The enhancement of the relative variation  $K$  can exceed  $10^5$ .

### A. Molecules with cancelation between hyperfine structure and rotational intervals

Consider diatomic molecules with the unpaired electron and the  $^2\Sigma$  ground state. Examples of such molecules include  $\text{LaS}$ ,  $\text{LaO}$ ,  $\text{LuS}$ ,  $\text{LuO}$ , and  $\text{YbF}$  [73]. The hyperfine interval  $\Delta_{\text{hfs}}$  is proportional to  $\alpha^2 Z F_{\text{rel}}(\alpha Z) \mu g_{\text{nuc}}$ , where  $F_{\text{rel}}$  is an additional relativistic (Casimir) factor [75]. The rotational interval  $\Delta_{\text{rot}} \propto \mu$  is roughly independent on  $\alpha$ . If we find a molecule with  $\Delta_{\text{hfs}} \approx \Delta_{\text{rot}}$ , the splitting  $\omega$  between hyperfine and rotational levels will depend on the following combination

$$\omega \propto \mu [\alpha^2 F_{\text{rel}}(\alpha Z) g_{\text{nuc}} - \text{const}]. \quad (39)$$

Relative variation is then given by

$$\frac{\delta\omega}{\omega} \approx \frac{\Delta_{\text{hfs}}}{\omega} \left[ (2 + K) \frac{\delta\alpha}{\alpha} + \frac{\delta g_{\text{nuc}}}{g_{\text{nuc}}} \right] + \frac{\delta\mu}{\mu}, \quad (40)$$

where the factor  $K$  comes from variation of  $F_{\text{rel}}(\alpha Z)$ , and for  $Z \sim 50$ ,  $K \approx 1$ . As long as  $\Delta_{\text{hfs}}/\omega \gg 1$ , we can neglect the last term in Eq. (40).

The data on hyperfine structure of diatomics are sparse and usually not very accurate. This hampers the search for molecules with strong cancelation of the types, discussed here. Using data from [73] one can find that  $\omega = (0.002 \pm 0.01) \text{ cm}^{-1}$  for  $^{139}\text{La}^{32}\text{S}$  [45]. Note that for  $\omega = 0.002 \text{ cm}^{-1}$  the relative frequency shift is:

$$\frac{\delta\omega}{\omega} \approx 600 \frac{\delta\alpha}{\alpha}. \quad (41)$$

With new data on molecular hyperfine constants appearing regularly, it is likely that other molecular candidates for such experiments will appear soon.

### B. Molecules with cancelation between fine-structure and vibrational intervals

The fine-structure interval  $\omega_f$  rapidly grows with the nuclear charge  $Z$ :

$$\omega_f \sim Z^2 \alpha^2, \quad (42)$$

On the contrary, the vibration energy quantum decreases with the atomic mass:

$$\omega_{\text{vib}} \sim M_r^{-1/2} \mu^{1/2}, \quad (43)$$

where the reduced mass for the molecular vibration is  $M_r m_p$ . Therefore, we obtain an equation  $Z = Z(M_r, v)$  for the lines on the plane  $Z, M_r$ , where we can expect approximate cancelation between the fine-structure and vibrational intervals:

$$\omega = \omega_f - v \omega_{\text{vib}} \approx 0, \quad v = 1, 2, \dots \quad (44)$$

Using Eqs. (42–44) it is easy to find the dependence of the transition frequency on the fundamental constants:

$$\frac{\delta\omega}{\omega} = \frac{1}{\omega} \left( 2\omega_f \frac{\delta\alpha}{\alpha} + \frac{v}{2} \omega_{\text{vib}} \frac{\delta\mu}{\mu} \right) \approx K \left( 2 \frac{\delta\alpha}{\alpha} + \frac{1}{2} \frac{\delta\mu}{\mu} \right), \quad (45)$$

where the enhancement factor  $K = \frac{\omega_f}{\omega}$  determines the relative frequency shift for the given change of fundamental constants. Large values of the factor  $K$  hint at potentially favorable cases for performing an experiment because it is usually preferable to have larger relative shifts. However, there is no strict rule that larger  $K$  is always better. In some cases, such as very close levels, this factor may become irrelevant [42]. Thus, it is also important to consider the absolute values of the shifts and compare them to the linewidths of the corresponding transitions.

Because the number of molecules is finite we can not have  $\omega = 0$  exactly. However, for many molecules we do have  $\omega/\omega_f \ll 1$  and  $|K| \gg 1$ . Moreover, an additional “fine tuning” may be achieved by selection of isotopes and rotational,  $\Omega$ -doublet, and hyperfine components. Therefore, we have two large manifolds, the first one is built on the electron fine-structure excited state, and the second one is built on the vibrational excited state. If these manifolds overlap, one may select two or more transitions with different signs of  $\omega$ . In this case expected sign of the  $|\omega|$ -variation must be different (since the variation  $\delta\omega$  has the same sign) and one can eliminate some systematic effects. Such control of systematic effects was used in Refs. [42, 43, 74] for transitions between close levels in two dysprosium isotopes. The sign of energy difference between two levels belonging to different electron configurations was opposite for the  $^{163}\text{Dy}$  and  $^{162}\text{Dy}$  transitions used in that work.

In Table I we present the list of molecules from Ref. [73] where the ground state is split in two fine-structure levels

TABLE I: Diatomic molecules with quasidegeneracy between the ground-state vibrational and fine-structure excitations. All frequencies are in  $\text{cm}^{-1}$ . The data are taken from Ref. [73]. Enhancement factor  $K$  is estimated using Eq. (45).

Molecule	Electronic states	$\omega_f$	$\omega_{\text{vib}}$	$K$
$\text{Cl}_2^+$	$^2\Pi_{3/2,1/2}$	645	645.6	1600
$\text{CuS}$	$^2\Pi$	433.4	415	24
$\text{IrC}$	$^2\Delta_{5/2,3/2}$	3200	1060	160
$\text{SiBr}$	$^2\Pi_{1/2,3/2}$	423.1	424.3	350

and Eq. (44) is approximately fulfilled. The molecules  $\text{Cl}_2^+$  and  $\text{SiBr}$  are particularly interesting. For both of them the frequency  $\omega$  defined by Eq. (44) is of the order of  $1 \text{ cm}^{-1}$  and comparable to the rotational constant  $B$ . This means that  $\omega$  can be reduced further by proper choice of isotopes, rotational quantum number  $J$  and hyperfine components. New dedicated measurements are needed to determine exact values of the transition frequencies and to find the best transitions. However, it is easy to find the necessary accuracy of the frequency-shift measurements. According to Eq. (45), the expected frequency shift is

$$\delta\omega = 2\omega_f \left( \frac{\delta\alpha}{\alpha} + \frac{1}{4} \frac{\delta\mu}{\mu} \right). \quad (46)$$

Assuming  $\delta\alpha/\alpha \sim 10^{-15}$  and  $\omega_f \sim 500 \text{ cm}^{-1}$ , we obtain  $\delta\omega \sim 10^{-12} \text{ cm}^{-1} \sim 3 \times 10^{-2} \text{ Hz}$ . In order to obtain similar sensitivity comparing hyperfine transition frequencies for Cs and Rb one has to measure the shift  $\sim 10^{-5} \text{ Hz}$ .

### C. Molecular ion $\text{HfF}^+$

The list of molecules in Table I is incomplete because of the lack of data in Ref. [73]. Let us briefly discuss one interesting case, which has been brought to attention quite recently. The  $\text{HfF}^+$  ion and other similar ions are being considered by E. Cornell’s group at JILA for an experiment to search for the electric dipole moment (EDM) of the electron [76, 77]. In this experiment, the ions are to be trapped in a quadrupole RF trap to achieve long coherence times. A similar experimental setup can be used to study possible time-variation of fundamental constants. A recent calculation by Petrov et al. [78] suggests that the ground state of this ion is  $^1\Sigma^+$  and the first excited state  $^3\Delta_1$  lies only  $1633 \text{ cm}^{-1}$  higher. The calculated vibrational frequencies for these two states are 790 and  $746 \text{ cm}^{-1}$ , respectively. For these parameters the vibrational level  $v = 3$  of the ground state is only  $10 \text{ cm}^{-1}$  away from the  $v = 1$  level of the  $^3\Delta_1$  state. Thus, instead of Eq. (44) we now have:

$$\omega = \omega_{\text{el}} + \frac{3}{2} \omega_{\text{vib}}^{(1)} - \frac{7}{2} \omega_{\text{vib}}^{(0)} \approx 0, \quad (47)$$



where superscripts 0 and 1 correspond to the ground and excited electronic states. The electronic transition with frequency  $\omega_{el}$  is not a fine-structure transition, and Eq. (42) is not applicable. Instead, by analogy with Eq. (6) we can write:

$$\omega_{el} = \omega_{el,0} + qx, \quad x = \alpha^2/\alpha_0^2 - 1. \quad (48)$$

In order to calculate the  $q$ -factor for  $\text{HfF}^+$  ion one needs to perform relativistic molecular calculations for several values of  $\alpha$ , which has not been done yet. However, it is possible to make an order of magnitude estimate using atomic calculation for the  $\text{Yb}^+$  ion [24]. According to Ref. [78], the  $^1\Sigma_1^+ - ^3\Delta_1$  transition, to a first approximation, corresponds to the  $6s - 5d$  transition in the hafnium ion. It is well known that valence  $s$ - and  $d$ -orbitals of heavy atoms have very different dependence on  $\alpha$ : while the binding energy of  $s$ -electrons grows with  $\alpha$ , the binding energy of  $d$ -electrons decreases [22, 23, 24, 25]. For the same transition in the  $\text{Yb}^+$  ion the Ref. [24] gives  $q_{sd} = 10000 \text{ cm}^{-1}$ . Using this value as an estimate, we can write by analogy with Eq. (45):

$$\frac{\delta\omega}{\omega} \approx \left( \frac{2q}{\omega} \frac{\delta\alpha}{\alpha} + \frac{\omega_{el}}{2\omega} \frac{\delta\mu}{\mu} \right) \approx \left( 2000 \frac{\delta\alpha}{\alpha} + 80 \frac{\delta\mu}{\mu} \right), \quad (49)$$

$$\delta\omega \approx 20000 \text{ cm}^{-1} (\delta\alpha/\alpha + 0.04\delta\mu/\mu). \quad (50)$$

Assuming  $\delta\alpha/\alpha \sim 10^{-15}$  we obtain  $\delta\omega \sim 0.6 \text{ Hz}$ .

#### D. Estimate of the natural widths of the quasidegenerate states

As we mentioned above, it is important to compare frequency shifts caused by time-variation of constants to the linewidths of corresponding transitions. First let us estimate the natural width  $\Gamma_v$  of the vibrational level  $v$ :

$$\Gamma_v = \frac{4\omega_{\text{vib}}^3}{3\hbar c^3} |\langle v|\hat{D}|v-1\rangle|^2. \quad (51)$$

To estimate the dipole matrix element we can write:

$$\hat{D} = \frac{\partial D(R)}{\partial R} \Big|_{R=R_0} (R - R_0) \sim \frac{D_0}{R_0} (R - R_0), \quad (52)$$

where  $D_0$  is the dipole moment of the molecule for equilibrium internuclear distance  $R_0$ . Using the standard expression for the harmonic oscillator,  $\langle v|x|v-1\rangle = (\hbar v/2m\omega)^{1/2}$ , we get:

$$\Gamma_v = \frac{2\omega_{\text{vib}}^2 D_0^2 v}{3c^3 M_r m_p R_0^2}. \quad (53)$$

For the homonuclear molecule  $\text{Cl}_2^+$   $D_0 = 0$  and expression (53) turns to zero. For the  $\text{SiBr}$  molecule, Eq. (53) gives  $\Gamma_1 \sim 10^{-2} \text{ Hz}$ , where we assume  $D_0^2/R_0^2 \sim 0.1 e^2$ .

Now let us estimate the width  $\Gamma_f$  of the upper state

of the fine-structure doublet  $^2\Pi_{1/2,3/2}$ . By analogy with Eq. (51) we can write:

$$\Gamma_f = \frac{4\omega_f^3}{3\hbar c^3} |\langle ^2\Pi_{3/2}|D_1|^2\Pi_{1/2}\rangle|^2. \quad (54)$$

The dipole matrix element in this expression is written in the molecular frame and we have summed over final rotational states. This matrix element corresponds to a spin-flip and turns to zero in the non-relativistic approximation. Spin-orbit interaction mixes the  $^2\Pi_{1/2}$  and  $^2\Sigma_{1/2}$  states:

$$|^2\Pi_{1/2}\rangle \rightarrow |^2\Pi_{1/2}\rangle + \xi |^2\Sigma_{1/2}\rangle, \quad (55)$$

and the matrix element in Eq. (54) becomes [79]:

$$\langle ^2\Pi_{3/2}|D_1|^2\Pi_{1/2}\rangle \approx \xi \langle \Pi|D_1|\Sigma\rangle \sim \frac{\alpha^2 Z^2}{10(E_\Pi - E_\Sigma)}, \quad (56)$$

where  $E_\Sigma$  is the energy of the lowest  $\Sigma$ -state. Substituting Eq. (56) into Eq. (54) and using energies from Ref. [73], we get the following estimate for the molecules  $\text{Cl}_2^+$  and  $\text{SiBr}$ :

$$\Gamma_f \sim 10^{-2} \text{ Hz}. \quad (57)$$

Here we took into account that the unpaired electron in  $\text{SiBr}$  molecule is predominantly located at Si ( $Z=14$ ) rather than at Br ( $Z=35$ ). Because of this, the fine-structure splitting in  $\text{SiBr}$  is smaller than that of  $\text{Cl}_2^+$ , where  $Z = 17$  (see Table I).

We conclude that natural widths of the molecular levels considered here are of the order of  $10^{-2} \text{ Hz}$ . This can be compared, for example, to the natural width 12 Hz of the level  $^2D_{5/2}$  of  $\text{Hg}^+$  ion, which was used in atomic experiment [4]. For such narrow levels the lifetime may depend on the interaction with the black body radiation [80]. According to this reference, the lifetimes of the ro-vibrational levels of polar molecules at room temperature vary from 1 s to 100 s.

## IX. EXPERIMENTS WITH $\text{Cs}_2$ AND $\text{Sr}_2$

In this section we discuss two recently proposed experiments with cold diatomic molecules. The first one with  $\text{Cs}_2$  molecule was proposed at Yale [44, 81] and the second experiment with  $\text{Sr}_2$  molecule is in preparation at JILA [82].

The Yale experiment is based on the idea [44] to match an electronic energy with a large number of vibrational quanta. The difference with Eqs. (42 – 44) is that here electronic transition is between the ground state  $^1\Sigma_g^+$  and the  $^3\Sigma_u^+$  state and, to a first approximation, its frequency is independent of  $\alpha$ . The energy of this transition is about  $3300 \text{ cm}^{-1}$  and the number of vibrational quanta needed to match this interval is on the order 100 (see Fig. 1). For the vibrational quantum number  $v \sim 100$  the density of

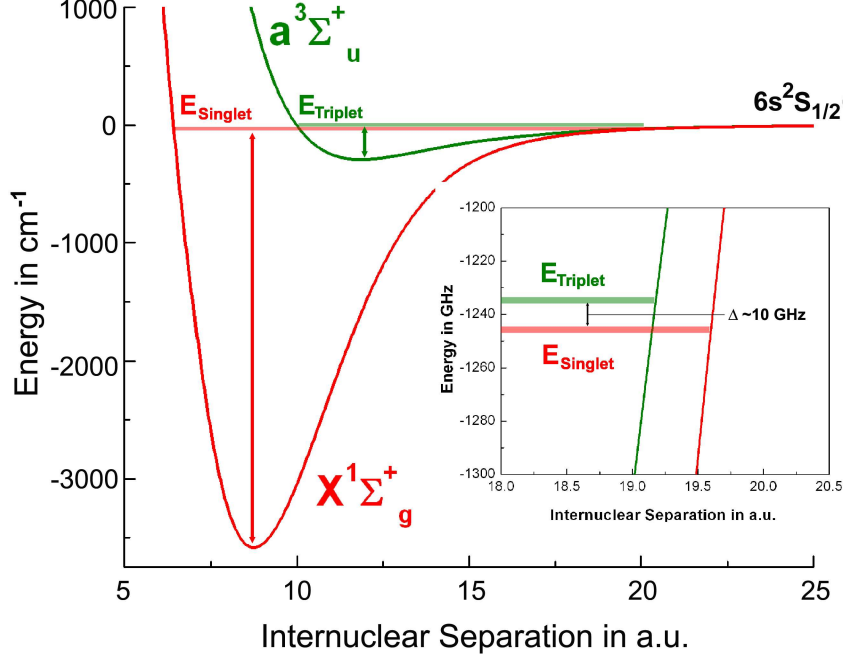


FIG. 1: Levels  $^3\Sigma_u^+$  and  $^1\Sigma_g^+$  in  $\text{Cs}_2$  molecule (figure from Ref. [83]).

levels is high due to unharmonicity and it is possible to find very close levels of two different potential curves. This leads to enhanced sensitivity to variation of  $\mu$ , as in Eq. (44). Cold  $\text{Cs}_2$  molecules can be produced in a particular quantum state by photoassociation of Cs atoms in a trap.

Let us estimate the sensitivity of this experiment to variation of  $\alpha$  and  $\mu$ . For the electronic transition energy we can use Eq. (48). If we neglect unharmonicity, we can write the transition frequency between close vibrational levels of the two electronic terms in the form

$$\omega = \omega_{\text{el},0} + qx + (v_2 + \frac{1}{2})\omega_{\text{vib},2} - (v_1 + \frac{1}{2})\omega_{\text{vib},1}, \quad (58)$$

where  $v_2 \ll v_1$ . The dependence of this frequency on constants is given by:

$$\delta\omega \approx 2q \frac{\delta\alpha}{\alpha} - \frac{\omega_{\text{el},0}}{2} \frac{\delta\mu}{\mu}, \quad (59)$$

where we took into account that  $\omega \ll \omega_{\text{el},0}$ . A very rough estimate of the factor  $q$  can be done in the following way. For the ground state of atomic Cs the  $q$ -factor is about  $1100 \text{ cm}^{-1}$ , which is close to  $\frac{1}{4}\alpha^2 Z^2 \varepsilon_{6s}$ , where  $\varepsilon_{6s}$  is the ground-state binding energy. If we assume that the same relation holds for the electronic transition in molecule, we get  $|q| \sim \frac{1}{4}\alpha^2 Z^2 \omega_{\text{el},0} \sim 120 \text{ cm}^{-1}$ . Using this estimate

and Eq. (59) we get:

$$\delta\omega \approx -240 \frac{\delta\alpha}{\alpha} - 1600 \frac{\delta\mu}{\mu}, \quad (60)$$

where we assume that relativistic corrections reduce dissociation energy of the molecule, so  $q$  is negative. This estimate shows that the experiment with  $\text{Cs}_2$  is mostly sensitive to variation of  $\mu$ .

Estimate (60) is obtained in the harmonic approximation. As mentioned above, for high vibrational states real potential is highly unharmonic. This significantly decreases the sensitivity of this experiment compared to the naive estimate (60). It can be easily seen either from the WKB approximation [44, 81], or from an analytical solution for the Morse potential [82]. Quantization condition for vibrational spectrum in the WKB approximation reads:

$$\int_{R_1}^{R_2} \sqrt{2M(U(r) - E_n)} dr = (v + \frac{1}{2})\pi. \quad (61)$$

Differentiating this expression in  $\mu$  we get:

$$\delta E_v = \frac{v + \frac{1}{2}}{2\rho(E_v)} \frac{\delta\mu}{\mu}, \quad (62)$$

where  $\rho(E_v) \equiv (\partial E_v / \partial v)^{-1} \approx (E_v - E_{v-1})^{-1}$  is the level density. For the harmonic part of the potential,  $\rho = \text{const}$

and the shift  $\delta E_v$  grows linearly with  $v$ , but for vibrational states near the dissociation limit the level density  $\rho(E) \rightarrow \infty$  and  $\delta E_v \rightarrow 0$ . Consequently, maximum sensitivity  $\sim 1000 \text{ cm}^{-1}$  is reached at  $v \approx 60$ , and rapidly drops for higher  $v$ . At present the group at Yale has found a conveniently close vibrational level of the upper  $^3\Sigma_u$  state for  $v = 138$ , but where the sensitivity is only  $\sim 200 \text{ cm}^{-1}$  [81]. There are still good chances that there are other close levels with smaller  $v$ , where the sensitivity may be several times higher.

It is important that because of unharmonicity, the sensitivity to variation of  $\alpha$  also decreases compared to the estimate (60). The reason for this is the following. For the highest vibrational levels of the ground state, as well as for all levels of the upper (weakly bound) state, the separation between nuclei is large,  $R \gtrsim 12 \text{ a.u.}$  (see Fig. 1). Thus, both electronic wave functions are close to either symmetric (for  $^1\Sigma_g^+$ ) or antisymmetric combination (for  $^3\Sigma_u^+$ ) of atomic  $6s$  functions:

$$\Psi_{g,u}(r_1, r_2) \approx \frac{1}{\sqrt{2}} (6s^a(r_1)6s^b(r_2) \pm 6s^b(r_1)6s^a(r_2)). \quad (63)$$

Therefore, all relativistic corrections are (almost) the same for both states.

Similar conclusions can be reached from the analysis of the Morse potential:

$$U_M(r) = d \left( 1 - e^{-a(r-r_0)} \right)^2 - d. \quad (64)$$

The eigenvalues for this potential are given by the analytical expression:

$$E_v = \omega_0 \left( v + \frac{1}{2} \right) - \frac{\omega_0^2 \left( v + \frac{1}{2} \right)^2}{4d}, \quad (65)$$

where  $\omega_0 = 2\pi a \sqrt{2d/M}$  and the last eigenvalue  $E_N$  is found from the conditions  $E_{N+1} \leq E_N$  and  $E_{N-1} \leq E_N$ . Obviously,  $E_N$  is very close to zero and is practically independent from any parameters of the model. Therefore, it is also insensitive to variation of constants.

We see that highest absolute sensitivity is reached for vibrational levels somewhere in the middle of the potential curve. However, in this part of the spectrum there are no close levels of different nature to maximize the relative sensitivity  $\delta\omega/\omega$ . One can still use frequency combs to perform high-accuracy measurements. This idea is used in the recent proposal by Zelevinsky *et al.* (author?) [82], who suggest to use an optical lattice to trap  $\text{Sr}_2$ . These molecules are formed by photoassociation in one of the uppermost vibrational levels of the ground electronic states (see Fig. 2). As we saw above, this level is not sensitive to the variation of  $\mu$ . At the next stage, a Raman transition is driven to one of the most sensitive levels in the middle of the potential well. This way it is possible to get the highest possible absolute sensitivity for a given molecule. Unfortunately, the dissociation en-

ergy for  $\text{Sr}_2$  is only about  $1000 \text{ cm}^{-1}$ , which is 3 times smaller than for  $\text{Cs}_2$ . Because of this, the highest sensitivity for the  $\text{Sr}_2$  molecule is about  $270 \text{ cm}^{-1}$ , i.e. only slightly higher than the sensitivity of the  $v = 138$  level in  $\text{Cs}_2$ . Therefore, it may be useful to try to apply this scheme to some other molecule with larger dissociation energy. Note that in the experiment with  $\text{Sr}_2$ , the sensitivity to  $\alpha$ -variation is additionally suppressed by a factor  $(38/55)^2 \approx 1/2$  because of the smaller  $Z$ .

## X. EXPERIMENTS WITH HYDROGEN MOLECULAR IONS $\text{H}_2^+$ AND $\text{HD}^+$

Hydrogen molecular ions are very attractive for fundamental studies because of their theoretical simplicity and experimental possibility of their cooling and trapping. Using  $\text{H}_2^+$  and  $\text{HD}^+$  ions for studying time-variation of electron-to-proton and proton-to-deuteron mass ratios  $\mu = m_e/m_p$  and  $m_p/m_d$  has been suggested in Refs. [84, 85]. Because of the unharmonicity, the ratio of the two vibrational transitions with very different vibrational quantum numbers is  $\mu$ -dependent [84]. There is no enhancement of the relative effect here, but the lines are very narrow and high-precision measurements are possible using frequency combs.

Recently  $\text{HD}^+$  ion has been cooled to 50 mK and trapped in a linear rf trap [86]. This allowed to measure the rovibrational transition  $v, N = 0, 2 \rightarrow v', N' = 4, 3$  with an absolute accuracy of 0.5 MHz. Using sensitivity coefficient from [85] one can see, that this accuracy translates in to  $5 \times 10^{-9}$  (5 ppb) accuracy for  $\mu$ . Note that modern molecular theory of  $\text{HD}^+$  has comparable accuracy [87]. Thus, a direct comparison between theory and experiment allows to determine the absolute value of  $\mu$  to 5 ppb.

## XI. CONCLUSIONS

We have seen that both diatomic and polyatomic molecules are used in astrophysics to study possible variation of the electron-to-proton mass ratio  $\mu$  on a time scale from 6 to 12 billion years. Results of these studies are inconclusive, see Eqs. (15), (19), and (36). The situation is similar for the astrophysical search for  $\alpha$ -variation. In principle, all these results can be explained by complex evolution of  $\mu$  and  $\alpha$  in space and time. Or, more likely, there are some systematic errors, which are not fully understood. Therefore it is extremely important to supplement astrophysical studies with laboratory measurements of present-day variation of these constants. This work is currently going on in many groups. Most of them use atomic frequency standards and atomic clocks. In this chapter we discussed several recent ideas and proposals on how to increase the sensitivity of laboratory tests by using molecules instead of atoms.

The only molecular experiment [47, 48], which has

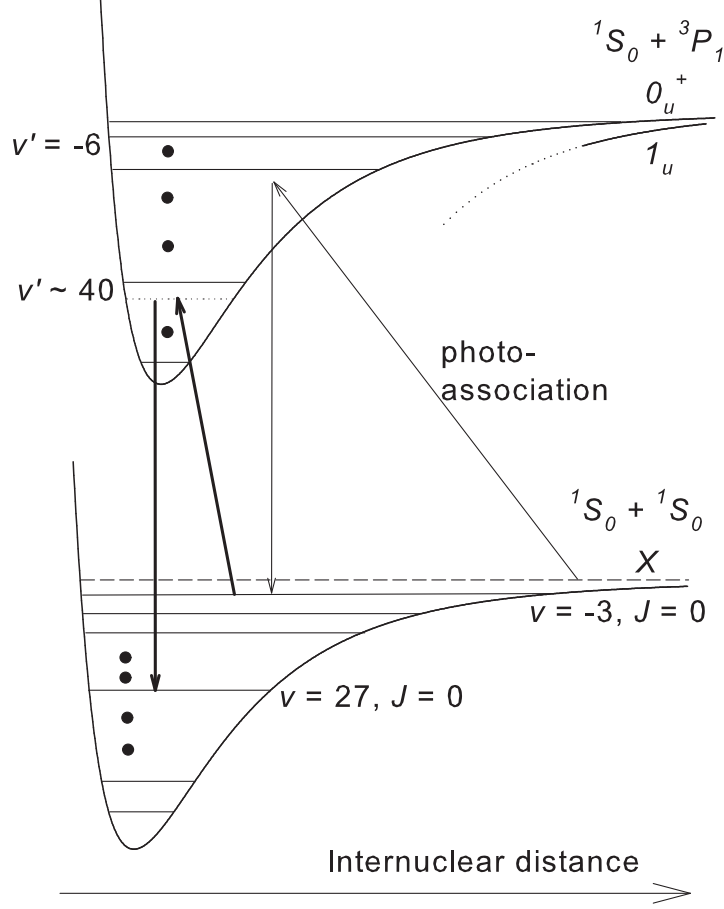


FIG. 2: The scheme for Raman spectroscopy of  $\text{Sr}_2$  ground-state vibrational spacings. A two-color photoassociation pulse prepares molecules in the  $v = v_{\text{max}} - 2$  vibrational state (denoted on the plot as  $v = -3$ ). Subsequently, a Raman pulse couples the  $v = -3$  and  $v = 27$  states via  $v' \approx 40$  level of the excited  $0_u^+$  state (figure from Ref. [82]).

reached the stage of placing the limit on the time-variation of fundamental constants (37), used a supersonic molecular beam of  $\text{SF}_6$ . Even though this experiment is less sensitive than the best atomic experiments, it constrains a different combination of fundamental constants. This allows to combine it with the results of atomic-clock experiments [4, 35, 37] to place the most stringent laboratory limit (38) on time-variation of  $\mu$ . The linewidth in this experiment,  $\Gamma \approx 200$  Hz, was determined by the time-of-flight through the 1-m Ramsey interferometer. A similar problem with the linewidth has prevented the use of the  $\text{ND}_3$  beam to perform competitive experiment on time-variation [46]. Using cold molecules would allow to reduce the linewidth by several orders of magnitude and drastically raise the sensitivity of molecular experiments.

We have seen that for such diatomic radicals as  $\text{Cl}_2^+$  and  $\text{SiBr}$  there are narrow levels of different nature separated by intervals  $\lesssim 1 \text{ cm}^{-1}$ . The natural widths of

these levels are on the order of  $10^{-2}$  Hz. This is comparable to the accuracy necessary to reach the sensitivity of  $\delta\alpha/\alpha \sim 10^{-15}$ , similar to that of the best modern laboratory tests. In the high-precision frequency measurements, the measurement accuracy is typically few orders of magnitude better than the linewidth. Of course, in order to benefit from such narrow lines, it is crucial to be able to cool and trap the molecules. In this respect the ion  $\text{Cl}_2^+$  looks more promising.

Even higher sensitivity to the temporal variation of  $\alpha$  can be found in  $\text{HfF}^+$  and similar molecular ions, which are being considered for the search of the electron EDM at JILA [76, 77, 78]. The transition amplitude between  $^3\Delta_1$  and  $^1\Sigma_0$  of  $\text{HfF}^+$  ion is also suppressed. The transition width is larger than for  $\text{Cl}_2^+$  and  $\text{SiBr}$  because of the larger value of  $Z$  and higher frequency  $\omega_f$ . In Ref. [78] the width of  $^3\Delta_1$  state was estimated to be about 2 Hz. This width is also of the same order of magnitude as the expected frequency shift for  $\delta\alpha/\alpha \sim 10^{-15}$ . At present

not much is known about these molecular ions. More spectroscopic and theoretical data are needed to estimate the sensitivity to  $\alpha$ -variation reliably. We hope that this review may stimulate further studies in this direction. Additional advantage here is the possibility to measure electron EDM and  $\alpha$ -variation using the same molecule and a similar experimental setup.

Preliminary spectroscopic experiment with the  $\text{Cs}_2$  molecule has been recently finished at Yale [81]. The electron transition in  $\text{Cs}_2$  goes between the  $^3\Sigma_u^+$  and  $^1\Sigma_g^-$  states, and, to a first approximation, is independent of  $\alpha$ . On the other hand the sensitivity to  $\mu$  may be enhanced because of the large number of vibrational quanta needed to match the electronic transition. However, the unharmonicity of the potential curve near the dissociation limit suppresses this enhancement for very high vibrational levels. As a result, the sensitivity to variation of  $\mu$  for the  $v = 138$  level is about the same as in Eq. (46). It is possible that there are other close levels with smaller vibrational quantum number  $v$  and, consequently, with higher sensitivity. Even if such levels are not found, the experiment with the  $v = 138$  level may improve present limit on variation of  $\mu$  by several orders of magnitude.

An experiment with the  $\text{Sr}_2$  molecule was recently proposed at JILA [82]. This experiment potentially has sim-

ilar sensitivity to variation of  $\mu$  as the experiment with  $\text{Cs}_2$  and both of them are complementary to the experiments with molecular radicals, which are mostly sensitive to  $\alpha$ -variation [49].

Finally, we have seen that the inversion spectra of such polyatomic molecules as  $\text{NH}_3$  and  $\text{ND}_3$  are potentially even more sensitive to variation of  $\mu$ . This has already been used in astrophysics to place the most stringent limit (36) on the time-variation of  $\mu$  on the cosmological timescale. Corresponding laboratory experiments require very slow molecular beams, fountains, or molecular traps. The work in this direction is going on [46].

To conclude this chapter, we see that this field is rapidly developing and new interesting results can be expected in the near future.

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